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Field emission of carbon nanotubes and electronic structure of carbon nanopeapods

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Abstract

We calculate the electron emission from nanostructures under an applied electric field using the ab initio pseudopotential method. The transition rates of the electrons are calculated by integrating the time-dependent Schrödinger equation for the states initially inside the emitter. A localized basis set is used for obtaining the eigenstates before emission and the potential that drives the field emission. The calculated electron-tunneling graph is quite linear in the short-time region, giving the transition rate within the simulation time. We have applied this new method to the field emission of carbon nanotubes as a test. Then we calculate the electronic structure of the fullerenes encapsulated inside the carbon nanotubes, the so-called carbon "nanopeapods". The fullerenes may or may not contain metallic atoms such as gadolinium or potassium. There is an interesting effect of strain when the diameter of the carbon nanotube is smaller than that of the inserted fullerene plus twice the van der Waals distance. © 2002 Published by Elsevier Science B.V.

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1. Field emission

In the former half of the present works, we carry out theoretical studies on field emission of carbon nanotubes. A strong electric field applied on the metal surface pulls out electrons from the metal via quantum-mechanical tunneling, which is called field emission. The analysis on the intensity of field-emitted electrons reveals valuable information such as electronic structures of the emitters or the variation of the work function depending on the surface condition [1]. On the practical side, the application to the flat panel display has provoked tremendous industrial interests [2]. The metal emitters used for the field emission are usually designed to have a sharp edge in order to enhance the local electric field at the tip and achieve a high rate of electron tunneling. The size of curvature of the emission tip has been typically around micrometers, but with the developments in the fabrication technology and the advent of new materials, the nanotip becomes available whose diameter is order of nanometers [3]. The nanotip is superior to the microtip in several ways. The most explicit advantage is the increase in the magnitude of the local electric field at the tip end, which results in the enhancement of the emission current compared to the microtip under the same external field. In addition, the low density of states at the tip makes the emitted electrons highly coherent and monoenergetic so that they can be used as an efficient source of the low-energy electron point source microscope [4]. The nanotip can be fabricated in situ with a field-ion technique on the metal surface. The local electric field greater than 1 V/Å rearranges the atoms that are mobile in the high temperature condition, producing a nanometric protrusion on the flat metal surface. On the other hand, there are also materials generically retaining the geometric sharpness down to a nanometer scale. For example, the diameter of the carbon nanotube is only a few nanometers while its length can be extended up to several micrometers.

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Owing to the high aspect ratio and the mechanical strength, the nanotube is a new material for electron emitters to be used in the field emission display [2] or as a coherent electron source [4].

The classical theory of field emission was developed by Fowler and Nordheim in 1928 [5]. In this story, the system is simplified as one-dimensional structure along the direction of the external field. The emission tip is modeled as a semi-infinite quantum well and the local electric field is approximated as a linear potential. The resulting current I is calculated with the WKB approximation and its functional dependence on the bias voltage (V) is

$$I \propto V^2 \exp\left(-\frac{\phi^{3/2}}{\beta V}\right), \tag{1}$$

where ϕ is the work function and β is a constant proportional to the field enhancement factor. In most experimental situations where the radius of curvature of the tip is greater than a micrometer, the I–V characteristics follow the form of Eq. (1), producing a straight F–N plot ($\ln(I/V^2)$ vs. $1/V$) and this is usually taken as evidence that the emission is driven by the field rather than by thermally excited electrons. The local electric field at the end of the tip is obtained from the slope of the F–N plot, using the known value of the work function. Such a simple picture, however, is not appropriate for the nanostructures. For instance, the boundary of the tip is not a well-defined physical quantity at the atomic scale and the potential obtained through the Laplace equation would not be valid for nanosized systems. In addition, one-dimensional WKB calculation neglects any spatial variation of the wave function in the xy-plane (the emission is assumed to be in the z-direction). The three-dimensional character of the wave function becomes very important in the nanotip in case that the xy-dimension of the tip is comparable to atomic distances. It is also well known that the emission current is changed significantly by the absorbate-induced states. The role of the localized states is pronounced for the nanotip because the atomic size of the tip restricts the number of channels for extended states. The localized states are difficult to consider in the semi-classical approach because they are not the normally current-carrying states. These theoretical arguments are reinforced by experiments for nanotips showing anomalous results that are not clearly explained by the F–N theory. In this work, we propose a conceptually new scheme targeted for simulating the field emission of the general nanosized systems. The full ab initio approach enables a detailed analysis based on the electronic structure of the emitter, which used to be beyond the scope of the theoretical methods. Important results have been published elsewhere in the literature [6,7].

2. Computational method

For the convenience of explanation, we divide the system into three non-overlapping regions along the emission direction: emitter (S_{emt}), barrier (S_{bar}), and vacuum (S_{vac}). The field emission process can be thought as the transmission of the electron from S_{emt} to S_{vac} by tunneling through S_{bar}. Two steps in our approach for studying the field emission of nanostructures are explained below. The first step is to obtain the self-consistent potential that drives the electron into the vacuum and the initial wave functions to be used in the time-evolution. This is accomplished by an ab initio calculation for a finite cluster imitating the tip region of the nanostructure including the uniform external field ($E_{\mathrm{ext}}\hat{z}$). We have used the localized orbitals in calculating the electronic structure with and without the external field. The self-consistent cycle is performed in order to accurately describe the effect of the external field. Because of the low computational cost in using the localized orbital, the size of model system can be very large. In addition, the confinement of the basis at the atomic sites naturally avoids the eigenstates located in S_{emt}. The second step is to evaluate the transition rate of the electrons from S_{emt} to S_{vac} with the potential calculated in the first step. As mentioned above, the wave functions described using the localized basis cannot extend into S_{vac} even if the potential is lower than in S_{emt}. We change the basis set to the plane waves and let the state evolve with time. The initial coefficients of plane waves are given by projecting the eigenstates onto a regular grid and executing the fast Fourier transformation. The Suzuki–Trotter type split-operator method is utilized for integrating the time-dependent Schrödinger equation [8]. The implementation into pseudopotential formalism follows the work by Sugino and Miyamoto [9]. Upon changing the basis to plane waves at $t > 0$, the electron starts to leak out of S_{emt} and the density begins to increase in S_{vac}. In order to evaluate the rate of electron leakage, we integrate the electron density over $z < z_0$ with z_0 efficiently defining a boundary plane ($z = z_0$) perpendicular to the electric field. z_0 is set to several angstroms outside the tip. Because of its incompleteness of localized basis, the eigenstates calculated in the first step are not exact even in S_{emt}. In order to avoid this problem, we find it necessary to introduce a relaxation step adjusting the wave function inside S_{emt} to the exact eigenstate before calculating the time evolution of the wave function. As a measure of the deviation from the exact eigenstate, we calculate the norm of the residual vector δ defined as

$$\delta = \langle R|R\rangle,$$

$$|R\rangle = (H' - \langle\psi|H'|\psi\rangle)|\psi\rangle, \tag{2}$$

where the normalization of $|\psi\rangle$ is assumed. The self-consistent Hamiltonian from the first step is utilized

with a strongly repulsive potential preventing the escape of the electron into the vacuum. For the original state in combination of localized orbitals, δ is about 0.5 a.u. and it is reduced below 0.005 a.u. through the direct inversion in the iterative subspace (DIIS) method with plane waves [10]. Since the DIIS method does not require information on other bands for minimizing the residual vector, the time-consuming orthogonalization process is avoided. We expect a linear behavior of the electronic leakage curve in the short time region, which will be actually demonstrated in the case of the emission of carbon nanotubes in the Symposium talk. Details will be published elsewhere. The slope in the linear region corresponds to the transition rate of the specific state into free electrons, which will ultimately hit the phosphor screen. Therefore, we propose that the total current of the realistic (semi-infinite) nanotip be calculated as follows:

$$I = e\sum_i O_i T_i, \tag{3}$$

where O_i is the occupation number of the ith eigenstate of the model tip and T_i is its transition rate estimated the electron leakage graph.

3. Electronic structure of carbon peapods

It has been well established that the strain put in the same direction as the tube axis can induce the bandgap change; for instance, a 4% strain for the $(15,1)$ tube reduces the gap by 60% [11], a substantial change in the electronic band structure. Recently, there are several experimental observations reported on the existence of fullerenes or metallo-fullerenes inside carbon nanotubes, the so-called carbon nanopeapods [12–14]. If the diameter of the carbon nanotube encapsulating fullerenes is smaller than that of inserted fullerene plus twice the van der Waals distance, it is possible that there is strain on the carbon nanotube and fullerenes, and the strain can alter the electronic structure. The charge distribution of the system may as well be changed under this condition. We have investigated the electronic structure of a few types of carbon nanopeapods in order to understand the behavior of electrons in the strained systems. Fig. 1 schematically shows a carbon nanopeapod (C_{82} encapsulated in a $(11,9)$ carbon nanotube). Expansion of the nanotube diameter by the large fullerene inside is illustrated. The degree of expansion is somewhat exaggerated for visual clarity. This is a case where fullerenes are packed rather sparsely inside the nanotube. This happens when the diameter of the fullerene is slightly greater than that of the nanotube minus twice the van der Waals distance, and it is an endothermic process when the mismatch is sufficiently large as shown in a theoretical study [15]. Experimentally, this kind of samples is produced when fullerenes and nanotubes are kept in a sealed glass ampoule at 500 °C for 24 h [16]. The density of the states (DOS) of the nanotubes with the fullerenes inside are shown in Fig. 2.

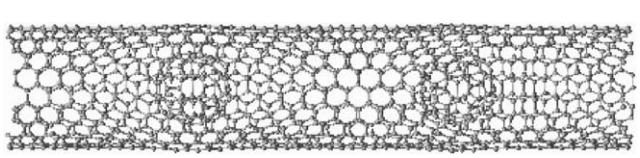

Fig. 1.

The distance between fullerenes is much longer than the typical van der Waals distance (~3.4 Å) because the fullerenes are not allowed to move freely to form densely packed peapod in the case we are interested. Therefore, the DOS here is essentially that of the isolated fullerene encapsulated in the tube without the interaction between fullerenes. Fig. 2(a) shows the DOS of C_{82} encapsulated in a $(12,8)$ carbon nanotube, and (b) shows that of C_{82} encapsulated in a $(17,0)$ nanotube. Comparison between the two indicates that the size of the energy gap (~0.5 eV) and other electronic structures are more or less similar. The states associated with C_{82} are located just below the Fermi level (zero of the energy) in both cases as indicated in dashed lines (between −0.2 and 0 eV). Since the $(17,0)$ tube has about the same diameter as the $(12,8)$ tube, the similarity of the gap is expected for unstrained nanotubes. However, a non-trivial result of our calculation is that the gap changes very little by the insertion of a relatively large-sized fullerene, C_{82}, into the $(12,8)$ or $(17,0)$ nanotube. According to the

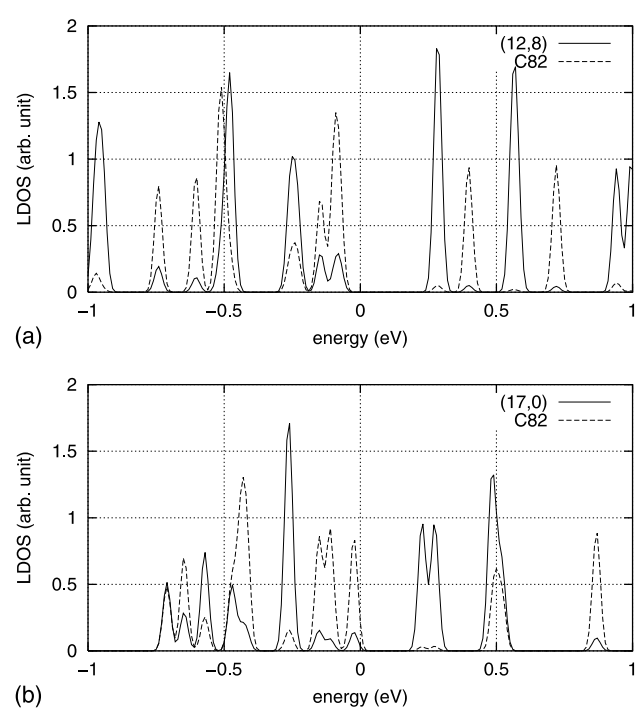

Fig. 2.

theory for nanotubes under large elongation along the tube axis, (n, m) nanotube experiences an increase of the gap when $n - m = 3k + 1$ is satisfied (n, m, and k are all integers). A $(12, 8)$ tube comes under this condition. On the other hand, the nanotube should exhibit a decrease of the gap when $n - m = 3k - 1$ is satisfied. Our calculations of the relaxed geometry show that the strain is very small (much less than 1% in either the axial or circumferential direction) and the energy gap remains naturally the same for both $(12, 8)$ and $(17, 0)$ nanotubes. Further calculations for various geometries are in progress. We believe that calculations covering all interesting cases of fullerenes encapsulated in nanotubes will shed light on physical behaviors and lead to useful applications of these newly emerging carbon nanopeapod systems.

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